CHEMICAL THERMODYNAMICS

Chemical thermodynamics deals with energy and its transformations in chemical systems. Students must recognize in both a qualitative and a quantitative sense the complex relationship between the spontaneity of a chemical reaction and its free energy, enthalpy, and entropy. Calculations involving changes in entropy, enthalpy, and free energy and their relationship to the equilibrium constant of a chemical reaction must be mastered. The important quantitative and qualitative relationships between thermodynamics, kinetics, and equilibrium are presented in Chapter 19 of *Chemistry the Central Science*.

19.1 **Spontaneous Processes**

19.2 **Entropy and the Second Law of Thermodynamics**

19.3 **The Molecular Interpretation of Entropy**

19.4 **Entropy Changes in Chemical Reactions**

19.5 **Gibbs Free Energy**

19.6 **Free Energy and Temperature**

19.7 **Free Energy and the Equilibrium Constant**

Chemical thermodynamics answers a fundamental question. Why does change occur?

The driving influences for any chemical and physical change are:

1. **Change in enthalpy, ΔH,** (heat transferred between the system and the surroundings).
2. **Change in entropy, ΔS,** (randomness or disorder of the system).

In general, chemical and physical systems tend to change in a direction that moves toward lower enthalpy (they release heat into the environment) and higher entropy (they become more random or disordered).

Sometimes these two influences are in direct conflict with each other and the reaction seeks a balance between moving toward lower enthalpy and higher entropy. Systems reach this balance at equilibrium.

Section 19.1   ## Spontaneous Processes

A **spontaneous change** is one that proceeds on its own without any outside assistance. A spontaneous change occurs in a definite direction. Processes that are spontaneous in one direction are nonspontaneous in the opposite direction. For example, a rock falls to the ground spontaneously. The opposite process, a rock rising from the ground, is nonspontaneous. Similarly, a campfire burns spontaneously. The "un-burning" of a campfire is nonspontaneous.

Review Section 5.3   ## Enthalpy

Recall from Topic 5 that **enthalpy** is the heat transferred between a chemical or physical system and its surroundings during a constant-pressure process.

The **change in enthalpy,** ΔH, is the **heat absorbed** by a system at constant pressure.

An **endothermic** process is one that absorbs heat from the environment. ΔH is positive.

An **exothermic** process is one that releases heat into the environment. ΔH is negative.

The **first law of thermodynamics,** also called the law of conservation of energy, states that in all cases energy is conserved. It can neither be created nor destroyed. This means that the amount of energy gained by a system must equal the amount of energy lost by the environment and vice versa.

A major driving influence for a chemical and physical change is the tendency for systems to move toward lower enthalpy by releasing energy into the environment. Thus exothermic processes, those that release energy into the environment, usually but not always are spontaneous. They proceed on their own without any outside assistance.

Recall from Section 5.7 of *Chemistry the Central Science* that the enthalpy change for a given reaction can be calculated from the enthalpies of formation for products minus the enthalpies of formation for reactants:

$$\Delta H^\circ_{rxn} = \Sigma \Delta H^\circ_{f\,products} - \Sigma \Delta H^\circ_{f\,reactants}$$

Entropy and the Second Law of Thermodynamics

Section 19.2

Entropy is best considered to be the extent of randomness or disorder in a chemical or physical system. For example, gases are more random than are liquids.

Kinetic molecular theory states that gases consist of a large number of atoms and/or molecules having a high kinetic energy so they are in continuous, random motion. The attractive forces between gas particles are negligible compared to their kinetic energy. (See Section 10.7.) In contrast, liquids have lower kinetic energy, and the attractive forces between the particles are sufficiently significant to hold the molecules together but still allow them to freely move past one another. Solids have relatively low kinetic energy, and the attractive forces work to lock the molecules into place, often in a very ordered crystal lattice. (See Section 11.1.) Gases, because of their relative disorder, have higher entropy than do liquids. Solids generally have lower entropy than either liquids or gases.

The **change in entropy, ΔS,** for any process is a measure of the change in randomness or disorder of the system. In general, as the phase of a given system changes from solid to liquid to gas, the entropy of the system increases and ΔS is positive for such changes. Phase changes from gas to liquid, gas to solid, or liquid to solid all happen with a decrease in entropy and ΔS is negative. Table 19.1 illustrates examples of entropy changes for various physical and chemical processes.

Table 19.1. Changes that increase entropy: ΔS is positive

In General, Entropy Increases When	Example
solids change to liquids or gases	$CO_2(s) \dashrightarrow CO_2(g)$
liquids change to gases	$H_2O(l) \dashrightarrow H_2O(g)$
solids dissolve in liquid solutions	$NaCl(s) \dashrightarrow Na^+(aq) + Cl^-(aq)$
the number of gas molecules increases	$2NH_3(g) \dashrightarrow N_2(g) + 3H_2(g)$
temperature increases	Water increases in temperature.
volume increases	A gas expands.
the number of particles increase	A rock is crushed.
two or more pure substances are mixed	Sugar dissolves in water.

Your Turn 19.1

When helium is released from a toy balloon, does the entropy of the system increase or decrease? Explain your answer. Write your answer in the space provided.

Section 19.3

The Molecular Interpretation of Entropy

Entropy also increases for substances with increasing molecular complexity. For example, under the same conditions, O_3 has a higher entropy than O_2 because it is more complex.

Your Turn 19.2

Under the same conditions of pressure and temperature, which has greater entropy, gaseous methane or gaseous propane? Explain. Which has greater entropy, steam or ice? Explain. Write your answers in the space provided.

The **second law of thermodynamics** states that any spontaneous change is always accompanied by an overall increase in entropy.

The **third law of thermodynamics** states that the entropy of a pure crystalline substance at absolute zero is zero. Upon heating, the entropy of a pure crystalline substance gradually increases. Continued heating brings upon a sharp increase in entropy upon melting and another marked increase upon boiling as illustrated in Figure 19.1.
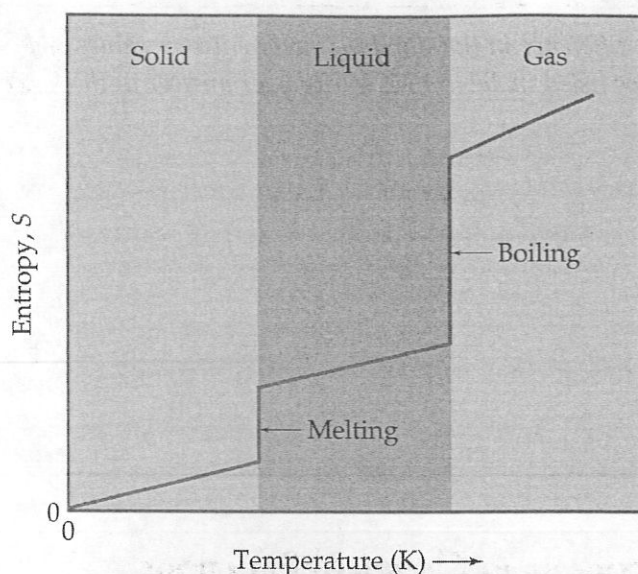
Figure 19.1. As the temperature of a substance increases, its entropy increases. Large changes in entropy are associated with phase changes.

Standard molar entropies, S°, are values for pure substances at one atmosphere pressure and 298 K. The units most often used for S° are J/mol K. Table 19.2 lists some examples. Notice than S° is comparatively larger for gases than for liquids or solids. Also, substances having the same phase but having higher molecular mass and/or higher molecular complexity, have higher entropy values. A more complete list of standard entropy values is given in Appendix C of *Chemistry the Central Science*.

Table 19.2. Standard molar entropies of selected substances at 298K

Substance	S°, kJ/mol K	Substance	S°, kJ/mol K
$I_2(s)$	116.73	$NO(g)$	210.62
$I_2(l)$	180.66	$NO_2(g)$	240.45
$I_2(g)$	260.57	$N_2O_4(g)$	304.30
$O(g)$	161.0	$H_2O(l)$	69.91
$O_2(g)$	205.0	$H_2O(g)$	188.83
$O_3(g)$	237.6		

Your Turn 19.3

Rationalize the difference in the standard molar entropy values of solid, liquid, and gaseous iodine as listed in Table 19.2. Write your answer in the space provided.

Section 19.4

Entropy Changes in Chemical Reactions

The change in entropy for a chemical reaction can be calculated by the following equation:

$$\Delta S°_{rxn} = \Sigma \, S°_{products} - \Sigma \, S°_{reactants}$$

Example:

What is the entropy change for the reaction, $2NO(g) + O_2(g)$ --→ $2NO_2(g)$?

Solution:

Substitute the entropy values listed in Table 19.2 into the equation. Don't forget to use the coefficients that balance the equation!

$$\Delta S°_{rxn} = \Sigma \, S°_{products} - \Sigma \, S°_{reactants}$$

$$\Delta S°_{rxn} = 2(240.45 \, J/mol \, K) - 205.0 \, J/mol \, K - 2(210.62 \, J/mol \, K)$$

$$\Delta S°_{rxn} = -145.34 \, J/mol \, K.$$

The answer is negative and makes sense because the system moves from three moles of gas to two moles of gas with a decrease in entropy.

Section 19.5

Gibbs Free Energy

Free energy (or **change in free energy, ΔG**) represents the amount of useful work that can be obtained from a process at constant temperature and pressure. Free energy, enthalpy, and entropy are related by the equation:

$$\Delta G = \Delta H - T\Delta S$$

ΔG is change in free energy measured in kJ/mol.

ΔH is change in enthalpy measured in kJ/mol.

ΔS is change in entropy measured in J/mol K.

T is absolute temperature in K.

The sign of ΔG tells if any given process is spontaneous as illustrated by Table 19.3.

Table 19.3. The sign of ΔG and spontaneity of reactions

If the ΔG Is	The Process Is
Negative ($-$)	spontaneous
Positive ($+$)	nonspontaneous (The reverse reaction is spontaneous.)
Zero (0)	at equilibrium

The change in free energy of a reaction can be calculated by the following equation: $\Delta G°_{rxn} = \Sigma \Delta G°_{f\,products} - \Sigma \Delta G°_{f\,reactants}$

The standard free energies of formation, $\Delta G°$, of various substances are listed in Appendix C of *Chemistry the Central Science*.

Example:

What is the standard free energy change for the reaction,

$2NO(g) + O_2(g) \dashrightarrow 2NO_2(g)$?
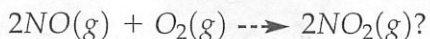
Solution:

Obtain the values of standard free energy of formation for each of the reactants and products from Appendix C of Chemistry the Central Science *and substitute them into the equation. Don't forget to take into account the number of moles of each substance as defined by the coefficients of the balanced equation.*

$\Delta G°_{rxn} = \Sigma G°_{products} - \Sigma G°_{reactants}$

$\Delta G°_{rxn} = 2(+51.58\ kJ/mol) - 0 - 2(+86.71\ kJ/mol)$

$= -70.26\ kJ/mol$

The sign of $\Delta G°$ for the reaction is negative, indicating that this is a spontaneous process at 298K.

Section 19.6   **Free Energy and Temperature**

What causes a process to be spontaneous? What influences chemical and physical change? The spontaneity of any process involves the two thermodynamic concepts, enthalpy and entropy. Often a balance exists between enthalpy and entropy, and temperature determines in which direction a reversible reaction will proceed spontaneously.

Phase change provides a good example. Consider the melting of ice and freezing of liquid water. Ice melts spontaneously at temperatures above 0°C and liquid water freezes spontaneously at temperatures below 0°C. Whether ice melts spontaneously or liquid water freezes spontaneously depends on the temperature.

Ice melts spontaneously at temperatures higher than 0°C because liquid water is more random than is solid water. The increase in entropy (the positive ΔS) as ice melts is the driving influence for the change from solid to liquid.

Liquid water freezes spontaneously at temperatures lower than 0°C because freezing is exothermic (ΔH is negative) and the move to lower enthalpy as liquid changes to solid influences the change.

$$H_2O(l) \dashrightarrow H_2O(s) + heat$$

At exactly 0°C, an equilibrium is established. At 0°C ice changes to liquid water at the same rate that liquid water changes to ice. At equilibrium, the drive toward lower enthalpy exactly balances the drive toward higher entropy.

The equation $\Delta G = \Delta H - T\Delta S$ and the signs of ΔH and ΔS are useful qualitatively to predict the spontaneity of any given reaction. It provides a model to guide our thinking in determining whether a reaction will be spontaneous or nonspontaneous. Table 19.4 illustrates.

Table 19.4. The effect of temperature on the spontaneity of reactions

ΔH	ΔS	$-T\Delta S$	ΔG	The Reaction Is:
−	+	−	−	Spontaneous at all temperatures
+	−	+	+	Nonspontaneous at all temperatures
−	−	+	+/−	Spontaneous only at low temperatures
+	+	−	+/−	Spontaneous only at high temperatures

When ΔH is negative and ΔS is positive, ΔG is always negative and the reaction is spontaneous at all temperatures because the reaction proceeds toward lower enthalpy and higher enthalpy.

If ΔH is positive and ΔS is negative, ΔG is always positive and the reaction is nonspontaneous at all temperatures. (However, the reverse reaction is spontaneous at all temperatures.)

Table 19.5 illustrates that often the change in free energy represents a balance between systems tending toward decreasing enthalpy and increasing entropy. If ΔH and ΔS both are positive, ΔG is negative only when the temperature is high enough for the entropy term to outweigh the enthalpy term. On the other hand, if ΔH and ΔS both are negative, ΔG is negative only when the temperature is low enough for the enthalpy term to outweigh the entropy term.

Table 19.5. A summary of important thermodynamic quantities

Quantity	Change in Enthalpy	Change in Entropy	Change in Free Energy
Symbol	ΔH	ΔS	ΔG
Unit	kJ/mol	J/mol K k	J/mol
Definition	Heat gained by a system	Change in randomness of a system	Available useful work
Comments	+ for endothermic − for exothermic	+ for increasing randomness − for decreasing randomness	+ for nonspontaneous − for spontaneous $\Delta G = 0$ at equilibrium

Your Turn 19.4

Is ΔG for a burning campfire positive or negative? Explain citing the positive or negative signs of ΔH and ΔS for the process. Is there a temperature at which ΔG for a burning campfire will change signs? Explain. Write your answers in the space provided.

Section 19.7   ## Free Energy and the Equilibrium Constant

The free energy change for any reaction under nonstandard conditions, ΔG, can be calculated from the standard free energy change, $\Delta G°$, by the following equation:

$$\Delta G = \Delta G° + RT \ln Q$$

ΔG = the free energy change under nonstandard conditions.

$\Delta G°$ = the free energy change under standard conditions: 25° C and one atmosphere partial presssure of all gases and 1 M concentration for all solutes.

R = 8.314 J/mol K, the ideal gas constant.

T = the absolute temperature in Kelvin.

Q = the reaction quotient.

Example:

Using standard free energies of formation for the reaction,

$2H_2S(g) + 3O_2(g) \dashrightarrow 2H_2O(g) + 2SO_2(g),$

calculate $\Delta G°$ and ΔG for a mixture at 25°C with the composition below.

$P_{H_2S} = 1.00\ atm$ $P_{H_2O} = 0.500\ atm$ $P_{O_2} = 2.00\ atm$
$P_{SO_2} = 0.750\ atm$

Solution:

Using the standard free energies of formation from Appendix C of Chemistry the Central Science, calculate $\Delta G°$ for the reaction.

$\Delta G°_{rxn} = \Sigma\ \Delta G°_{products} - \Sigma\ \Delta G°_{reactants}$

$\Delta G°_{rxn} = 2(-300.4) + 2(-228.57) - 2(-33.01) - 0$

$\Delta G°_{rxn} = -991.9\ kJ$

Evaluate Q and use the equation, $\Delta G = \Delta G° + RT \ln Q$, to calculate ΔG.

$Q = P^2_{SO_2}\ P^2_{H_2O}/P^2_{H_2S}\ P^3_{O_2} = (0.750)^2(0.500)^2/(1.00)^2(2.0)^3$
     $= 0.0176$

$\Delta G = \Delta G° + RT \ln Q =$

$-991.9\ kJ + (8.314\ J/mol\ K)(298\ K) \ln (0.0176)(1\ kJ/1000\ J)$
     $= -1002\ kJ$

Common misconception: When using the equation, $\Delta G = \Delta G° + RT \ln Q$, keep in mind that $\Delta G°$ is usually given in kJ whereas R is in units of J/mol K. Be sure to convert J to kJ using 1 kJ = 1000 J.

The standard free energy for any reaction is related to the equilibrium constant. At equilibrium, $\Delta G = 0$ and $Q = K$, the equilibrium constant. At equilibrium,

$$\Delta G° = -RT \ln K$$

Example:

The standard free-energy change for the following reaction at 25°C is −118.4 kJ/mol:

$KClO_3(s) \dashrightarrow KCl(s) + 3/2\ O_2(g)$

Calculate Kp for the reaction at 25°C and the equilibrium pressure of O_2 gas.

Solution:

$\Delta G° = -RT \ln K$

$-118.4\ kJ/mol = -(8.314\ J/mol\ K)(298\ K)(1\ kJ/1000\ J)\ \ln K_p$

$\ln Kp = 47.8$

$Kp = e^{47.8} = 5.68 \times 10^{20}$

$Kp = P^{3/2}_{O_2}$

$P_{O_2} = Kp^{2/3} = (5.68 \times 10^{20})^{2/3} = 6.9 \times 10^{13}\ atm$

Multiple Choice Questions

1. The standard free energy of formation, $\Delta G°_f$, for sodium chloride is the free energy change for which of the following reactions?

    A) $Na^+(g) + Cl^-(g) \rightarrow NaCl(g)$

    B) $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$

    C) $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$

    D) $Na(s) + 1/2Cl_2(g) \dashrightarrow NaCl(s)$

    E) $2NaCl(s) \dashrightarrow 2Na(s) + Cl_2(g)$

2. For which of these processes is the value of ΔS expected to be negative?

    I.   NaCl is dissolved in water.

    II.   Steam condenses to liquid water.

    III. $MgCO_3$ is decomposed into MgO and CO_2.

    A) I only

    B) I and III only

    C) II only

    D) II and III only

    E) I and II only

3. What are the signs of the enthalpy change and entropy change for the melting of ice?

    $H_2O(s) \rightarrow H_2O(l)$

	$\Delta H°$	$\Delta S°$
A)	+	+
B)	−	−
C)	−	+
D)	+	−
E)	0	0

4. Under which set of conditions does a temperature exist at which equilibrium can be established with all reactants and products in standard states?

    I. ΔS is +, ΔH is +

    II. ΔS is −, ΔH is −

    III. ΔS is +, ΔH is −

A) I only

B) II only

C) III only

D) I and II only

E) I and III only

5. Which of the following substances is expected to have the largest standard molar entropy?

A) $H_2O(s)$

B) $H_2O(l)$

C) $H_2O(g)$

D) $H_2O_2(l)$

E) $H_2O_2(g)$

6. In which process would ΔG be expected to be positive?

A) melting ice at $-10°C$ and 1.0 atm pressure

B) water evaporating at 25°C into dry air

C) cooling hot water to room temperature

D) sublimation of dry ice (solid carbon dioxide) at 25°C

E) a burning campfire

7. Which is not expected to have a value of zero?

A) $\Delta H°_f$ for $O_2(g)$

B) $\Delta G°_f$ for $K(s)$

C) S for $Ca(s)$ at 0 K

D) $\Delta H°_f$ for $Br_2(l)$

E) $\Delta G°_f$ for $O(g)$

8. Which process is exothermic and occurs with a decrease in entropy?

A) $H_2O(l) \dashrightarrow H_2O(s)$

B) $H_2O(s) \dashrightarrow H_2O(l)$

C) $H_2O(s) \dashrightarrow H_2O(g)$

D) $2H_2O(l) \dashrightarrow 2H_2(g) + O_2(g)$
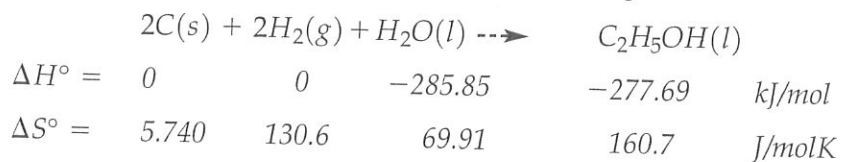
E) $H_2O(l) \dashrightarrow H_2O(g)$

9. In order to calculate the entropy change for the following reaction at 25°C and one atmosphere, what additional thermodynamic information is needed?

$$C(\text{solid graphite}) + O_2(g) \dashrightarrow CO_2(g)$$

A) $\Delta H°_f$ for $CO_2(g)$

B) $\Delta G°_f$ for $CO_2(g)$

C) $\Delta H°_f$ and $\Delta G°_f$ for $CO_2(g)$

D) $S°$ for $CO_2(g)$

E) $\Delta H°_f$ and $\Delta G°_f$ for both $C(\text{solid graphite})$ and $O_2(g)$

10. For a certain reaction, $\Delta H° = -150$ kJ/mol and $\Delta S° = -50$ J /mol K. Which of the following statements is true about the reaction?

A) It is spontaneous at high temperatures only.

B) It is spontaneous at low temperatures only.

C) It is spontaneous at all temperatures.

D) It is nonspontaneous at all temperatures.

E) There is no temperature at which the reaction will reach equilibrium.

Free Response Questions

1. At 25°C the equilibrium constant, Kp, for the reaction below is 0.281 atm.

$$Br_2(l) \rightarrow Br_2(g)$$

a. Calculate $\Delta G°$ for this reaction.

b. It takes 193 joules to vaporize 1.00 gram of $Br_2(l)$ at 25°C and 1.00 atmosphere pressure. Calculate $\Delta H°$ at 298 K.

c. Calculate $\Delta S°$ at 298 K for this reaction.

d. The normal boiling point of a liquid is the temperature at which the liquid and its vapor are at equilibrium at 1 atm pressure. Calculate the normal boiling point of bromine. Assume that $\Delta H°$ and $\Delta S°$ remain constant as the temperature is changed.

e. What is the equilibrium vapor pressure of bromine in torr at 25°C?

2. In principle, ethanol can be prepared by the following reaction.

	$2C(s)$	$+\ 2H_2(g)$	$+\ H_2O(l) \dashrightarrow$	$C_2H_5OH(l)$	
$\Delta H° =$	0	0	-285.85	-277.69	kJ/mol
$\Delta S° =$	5.740	130.6	69.91	160.7	J/molK

a. Calculate the standard enthalpy change, $\Delta H°$, for the reaction above.

b. Calculate the standard entropy change, $\Delta S°$, for the reaction above.

c. Calculate the standard free energy change, $\Delta G°$, for the reaction above at 298 K.

d. Calculate the value of the equilibrium constant, Kp at 25°C for the reaction above.

e. Calculate the partial pressure of $H_2(g)$ at equilibrium.

Additional Practice in *Chemistry the Central Science*

For more practice answering questions in preparation for the Advanced Placement examination try these problems in Chapter 19 of Chemistry the Central Science:

Additional Exercises: 19.84, 19.86, 19.89, 19.92, 19.94.

Integrative Exercises: 19.100, 19.101, 19.103, 19.104, 19. 105, 19.106.

Multiple Choice Answers and Explanations

1. D. The standard free energy of formation is the free energy change of a formation reaction, one that forms one mole of a substance from its component elements in their most stable forms. Solid sodium and gaseous diatomic chlorine are the most stable forms of those elements.

2. C. A negative ΔS denotes a change from a more random state to one of more order. In general, solids are more ordered than liquids which are more ordered than gases. Liquid water is more ordered than is steam. When solid NaCl dissolves in liquid water, it dissociates into more random aqueous ions in the liquid phase. Carbon dioxide gas is more random than solid magnesium carbonate.

3. A. All solids melt endothermically (where $\Delta H°$ is positive) because solids must absorb energy to overcome the strong attractive forces that hold the particles together. All solids melt with an increase in entropy (where $\Delta S°$ is positive) because liquids are more random than solids.

4. D. The fundamental thermodynamic condition at equilibrium is when ΔG is zero. At equilibrium, the equation $\Delta G = \Delta H - T\Delta S$ becomes $\Delta H = T\Delta S$. Because T is the absolute temperature in Kelvin, it must be positive. A positive temperature can only exist when the signs of ΔH and ΔS are both negative or both positive.

5. E. Entropy is the degree of randomness or disorder of a system. Gases have higher entropies than liquids which have higher entropies than solids. Additionally, when comparing substances having the same phase, the more complex the substance the higher is its entropy because complex substances have more possible rotational and vibrational modes of motion.

6. A. ΔG is positive for nonspontaneous processes. When determining qualitatively the sign of ΔG, ask the question: left on its own does it happen? If the answer is yes, the process is spontaneous and the sign of ΔG is negative. If the answer is no, the process is nonspontaneous and the sign of ΔG is positive. Ice will not melt spontaneously at $-10°C$ unless it is under pressure. ΔG is negative for all the other processes listed because left on their own, they will happen spontaneously.

7. E. $O(g)$ is not the most stable form of oxygen so its standard free energy is nonzero. Standard heats of formation, $\Delta H°_f$, and standard free energies of formation, $\Delta G°_f$, are zero for elements in their most stable form at $25°C$. The most stable forms of oxygen, potassium, and bromine are $O_2(g)$, $K(s)$, and $Br_2(l)$, respectively. The third law of thermodynamics states that the entropy, S, of a pure crystalline substance at absolute zero is zero. $Ca(s)$ at 0 K has $S = 0$.

8. A. In general, gases have more entropy than liquids and liquids have more entropy than solids. Phase changes from gas to liquid, gas to solid, and liquid to solid all are exothermic (release heat to the environment) and occur with a decrease in entropy (result in less random, more ordered products). The decomposition of liquid water to form gaseous products is endothermic and takes place with a large increase in entropy.

9. C. The given reaction is the formation reaction for $CO_2(g)$. Therefore, the values for $\Delta H°_f$ and $\Delta G°_f$ for $CO_2(g)$ are the same as the values for $\Delta H°_{rxn}$ and $\Delta G°_{rxn}$ for $CO_2(g)$. ΔS_{rxn} can be calculated using the equation, $\Delta G°_{rxn} = \Delta H°_{rxn} - T\,\Delta S°_{rxn}$. The given Celsius temperature must be converted to Kelvin. $\Delta H°_f$ and $\Delta G°_f$ for neither C(solid graphite) nor $O_2(g)$ are necessary because both are elements in their most stable forms so their values are each, by definition, zero.

10. B. Use the equation, $\Delta G = \Delta H - T\Delta S$, to guide your thinking. To be spontaneous requires a negative ΔG and that can only be achieved if the absolute value of the negative ΔH term is larger than the absolute value of the $T\Delta S$ term. At low temperatures ΔG will be negative. At high temperatures it will be positive. There is a temperature at which ΔG will be zero and the system will reach equilibrium.

Answers to Free Response Questions

1. a. $\Delta G° = -RT \ln K = -(8.314 \ J/mol \ K)(25 + 273 \ K) \ln (0.281)$

    $\Delta G° = 3.15 \ kJ/mol$

    b. $x \ kJ/mol = (193 \ J/g)(160 \ g/mol)(1 \ kJ/1000 \ J) = 30.9 \ kJ/mol$

    c. $\Delta G° = \Delta H° - T\Delta S°$

    $\Delta S° = (\Delta H° - \Delta G°)/T = (30.9 - 3.15)/298 \ K$
    $= .0931 \ kJ/mol \ K = 93.1 \ J/mol \ K$

    d. *The boiling point is the temperature at which the equilibrium vapor pressure of bromine equals the external pressure. Because the system is at equilibrium,* $\Delta G = 0$.

    $\Delta G = \Delta H - T\Delta S$

    $0 = 30.9 \ kJ/mol - T(.0931 \ kJ/mol \ K)$

    $T = 30.9/.0931 = 332 \ K$

    e. $Kp = P_{Br_2}(g)$

    $Kp = (0.281 \ atm)(760 \ torr/atm) = 214 \ torr$

2. a. $\Delta H°_{rxn} = \Sigma \ \Delta H°_{f \ products} - \Sigma \ \Delta H°_{f \ reactants}$
    $= -(-285.85) + (-277.69) = +8.16 \ kJ/mol$

    b. $\Delta S°rxn = \Sigma S°_{products} - \Sigma S°_{reactants}$
    $= +160.7 - 69.91 - 2(130.6) - 2(5.740) = -181.9 \ J/mol \ K$

    c. $\Delta G°_{rxn} = \Delta H°_{rxn} - T\Delta S°_{rxn}$

    $\Delta G°_{rxn} = +8.16 \ kJ/mol - (298K)(-181.9 \ J/mol \ K)$

    $/(1 \ kJ/1000 \ J) = +62.4 \ kJ/mol$

    $\Delta G° = -RT \ln K$

    $\ln K = -(+62.4 \ kJ/mol)/(8.314 \ J/mol \ K)(1 \ kJ/1000 \ J)$

    $(298 \ K) = -25.2$

    $K = -25.2 = 1.14 \times 10^{-11}$

    d. $Kp = P^{-2}_{H_2}$

    $P_{H_2} = Kp^{-1/2} = (1.14 \times 10^{-11})^{-1/2} = 2.96 \times 10^5 \ atm$

Answers to Your Turn

19.1. *Entropy of the system increases when helium is released from a toy balloon because the gas from the balloon mixes with the gases in the atmosphere, causing an increase in randomness or disorder.*

19.2. *Propane, $CH_3CH_2CH_3$, has greater entropy than methane, CH_4, because the molecules of propane are much more complex than the molecules of methane.*

Steam has more entropy than ice because gases are more random and disordered than are solids.

19.3. *Gaseous iodine has a higher standard molar entropy than either liquid or solid iodine because gases are more random than liquids or solids. Liquid iodine has a higher value than solid iodine because liquids are more random than solids.*

19.4. *A burning campfire is a spontaneous process where ΔG is negative. For the process, ΔH is negative and ΔS is positive so ΔG is negative at all temperatures. Thus, a burning campfire will never become nonspontaneous.*